

Decomposition of Clofibric Acid in Aqueous Media by Advance Oxidation Techniques: Kinetics Study and Degradation Pathway

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Summary: This study investigates the decomposition of clofibric acid (CLF) by different advanced oxidation processes (AOPs), such as UV (254nm), VUV (185 nm), UV / TiO₂ and VUV / TiO₂. The removal efficiencies of applied AOPs were compared in the presence and absence of dissolved oxygen. The removal efficiency of the studied AOPs towards degradation of CLF were found in the order of VUV / TiO₂ + O₂ > VUV/TiO₂ + N₂ > VUV alone > UV / TiO₂ + O₂ > UV / TiO₂ +N₂ > UV alone. The decomposition kinetics of CLF was found to follow *pseudo*-first order rate law. VUV / TiO₂ process was found to be most cheap and effective one for decomposition of CLF as compared to other applied AOPs in terms of electrical energy per order. Degradation products resulting from the degradation processes were also investigated using UPLC-MS /MS, accordingly degradation pathway was proposed.

Keywords: Clofibric acid, Advance Oxidation Processes (AOPs), Decomposition kinetics, UPLC – MS /MS, Wastewater.

Introduction

Recently, many studies have been reported on the high-consumption of pharmaceuticals and their occurrence in the environmental matrices at very low concentrations [1]. Among such pharmaceuticals, clofibric acid (CLF) (2-(4-chlorophenoxy)-2-methylpropanoic acid) is a widely used as blood lipid regulatory agent with therapeutic doses of about 1-2 g d⁻¹ per person, since they decrease the plasmatic concentration of cholesterol and triglycerides [2, 3]. Clofibric acid is resistant to degradation because of its polar nature. CLF is detected in the concentrations of 1 up to 10 µg L⁻¹ in sewage treatment plants, ground and drinking water [2, 4-6]. Advanced oxidation processes (AOPs) have recently emerged as an important class of technologies for the destruction of wide range of organic contaminants in water and waste water [7-10]. The AOPs are based on oxidizing radicals, mainly hydroxyl radicals, while other radicals and active oxygen species such as superoxide radical anions (⁻O₂), hydroperoxy radicals (HO₂[•]), triplet oxygen (³O₂) and organic peroxy radicals (R-O-O[•]) are also involved [10]. [•]OH- radical is found to be a very strong oxidant with oxidation potential of 2.8 eV and can react with variety of pollutants at a very high reaction rate of 10⁸ - 10¹⁰ M⁻¹s⁻¹ [11]. Heterogeneous photocatalysis, an advanced oxidation process, has been widely studied for the removal of wide range of pollutants from water and air [12]. The basic mechanism of heterogeneous photocatalysis involves

absorption of light with energy larger than band gap of semiconductor photocatalyst (for TiO₂, λ >387.5 nm), an electron is ejected from the ground valence band to the higher conduction band. However, it has been observed that the photocatalytic oxidation processes are of low efficiency, and it takes long time and thus results in high cost to purify water or air. To enhance the efficiency of photocatalytic oxidation process, many studies have been reported [13, 14]. Furthermore, strong oxidants such as ozone [15], hydrogen peroxide [16], persulfate ion [17] or periodate [16] were added in the reaction system to increase the overall decomposition rate.

Photolysis of water using vacuum ultraviolet light (VUV, λ < 200nm) is another means to generate hydroxyl radicals. In case of VUV-irradiation, water itself is homolyzed into hydrogen atom and hydroxyl radical, and other oxidative species such as hydrogen peroxide is also expected to be formed simultaneously [18]. This process recently received much attention for the decomposition of persistent organic pollutants.

In the present study the decomposition of CLF was investigated by various advance oxidation techniques. The main objectives of the present study were to (i) compare the removal efficiencies of UV, VUV, UV/TiO₂, VUV/ TiO₂ in the presence and absence of dissolved oxygen (ii) to investigate the

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decomposition kinetics of the applied AOTs and (iii) to investigate the practical applications of the applied AOTs towards removal of pharmaceuticals from wastewater.

Experimental

CHEMICALS AND REAGENTS. Clofibrac acid (CLF) was purchased from Sigma Aldrich (98%; CAS: 882-09-7). For the HPLC analysis acetic acid (Scharlau), methanol (Scharlau) and acetonitrile (Scharlau) were used as mobile phase. The solutions were prepared using Milli-Q water produced by MILLIPORE (resistivity: $18 \text{ M}\Omega \text{ cm}^{-1}$).

The effect of oxygen was investigated by bubbling O_2 - or N_2 -gases (purity = 99.999 %) through sample solutions. All the experiments were performed in triplicate.

Synthesis of TiO_2 / Ti Film. TiO_2 film was synthesized according to previously reported study from our research group [19]. Tetraorthotitanate, acetyl acetone, water and n-propanol was mixed together in a ratio of 1:0.3:0.4:7 to prepare a homogenous solution. The titanium sheet, pretreated with 10 % wt oxalic acid, was then dipped into the above prepared solution and then withdrawn at a speed of 1 mm s^{-1} . The dried TiO_2 film was then annealed in air at 500°C for 1 h at a heating rate of 2°C min^{-1} prior to photocatalytic procedures.

Characterization. To examine the morphology of synthesized TiO_2 / Ti films, field emission scanning electron microscopy was carried out on FE-SEM, S-5500, Hitachi, second electron resolution: $0.4 \text{ nm} / 30 \text{ kV}$ at accelerating voltage of 5.0 kV . X-ray diffraction analysis was carried out on Rigaku D/max-RB using k_α radiations at $\lambda = 0.154 \text{ nm}$. X-ray photoelectron spectroscopy was carried out to examine the chemical states of TiO_2 surface, using $\text{Al } k_\alpha$ as an exciting x-ray source.

Photochemical Reactor. The experiments were carried out in a cylindrical photo reactor (Fig. 1), having total capacity of 150 mL sample solution. UV / VUV lamp was inserted in the middle of the photo reactor, where cold water was continuously circulated through photo reactor to keep the temperature of the reactor at ambient conditions. A plate of TiO_2 / Ti catalyst was placed inside the photo reactor having CLF sample solution. In order to prepare oxygen-free and solutions saturated with molecular oxygen, nitrogen or oxygen gas was bubbled (flow rate = 50 mL min^{-1}) through the solution from the bottom of the photo reactor.

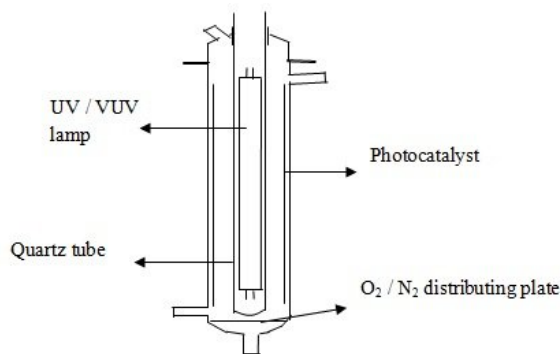


Fig. 1: Diagram of photo - reactor for evaluating the photocatalytic activity.

Irradiation Sources. Both UV and VUV lamps used were low-pressure mercury vapor lamps supplied by Cnlight Co. Ltd, China and had same power (15W) and identical appearance size. One lamp emits 254 nm UV light (referred as UV), and other emits 185 nm vacuum UV light (referred as VUV). The lamp was placed in the centre of the photo reactor with quartz tube protection (external diameter 25mm), the distance from the inner wall of the photo reactor to the external wall of the quartz tube was 15 mm.

Analysis

High Performance Liquid Chromatography. During the degradation experiments, the samples were analyzed using an Agilent 1200 series high performance liquid chromatography. A mobile phase of a 50-50% mixture of water-ethanol was used. The separation of the degradation products was carried out on a C18 Agilent column at 1 mL min^{-1} flow rate. The detection wavelength was 230 nm.

Ultra-Performance Liquid Chromatography With Tandem Mass Spectrometry. For determinations of the organic by-products, CLF was analysed on UPLC- MS / MS. The parent ion m/e 213.20, daughter ion m/e 127.30, cone voltage (22 V), and collision energy (15 eV) were used for CLF detection. Full scan mode was applied for acquiring complete informations about intermediates. CLF samples at different irradiation times were injected into mass spectrometer ion source by pure methanol with cone voltage of 10 V.

Pseudo-First Order Kinetic Model. To study the decomposition kinetics of CLF under various applied AOPs, pseudo-first order kinetics was applied as presented in equation (1):

$$\ln (C_0 / C) = kt \quad (1)$$

where “ C_0 ” represents initial concentration of CLF and “ C ” represents concentration of CLF after time “ t ”. k is the apparent rate constant.

The half-life ($t_{1/2}$) was calculated from the rate constant equation as shown below:

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

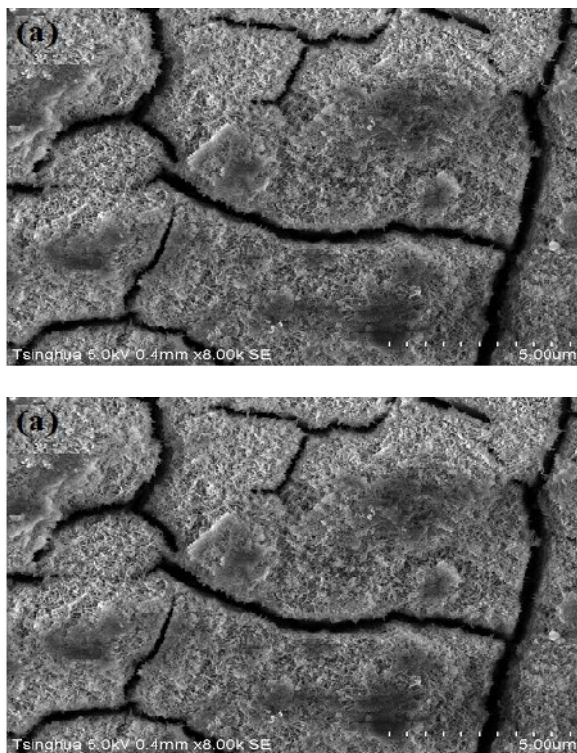


Fig. 2: FESEM images of TiO_2 films grown on Ti – substrate.

Results and Discussion

Control experiments conducted in the presence of TiO_2 and without irradiation reveals that CLF concentration was not significantly affected by passing O_2 / N_2 gasses or by TiO_2 absorption after being kept in dark for 30 min.

Structure and Morphology of Synthesized TiO_2 / Ti Film

Fig. 2 shows FESEM images of TiO_2 films fabricated on Ti – substrate. It can be seen that TiO_2 particles are tightly and uniformly attached to the Ti-

substrate. XRD pattern of synthesized TiO_2 / Ti films is shown in Fig. 3 and is well matched with JCPDS card no. 21-1272 suggesting high phase purity of anatase TiO_2 . Some rutile character was also observed in our XRD pattern which might be coming from Ti – substrate on which TiO_2 film was directly grown. XPS spectra of TiO_2 films grown on Ti-substrate are shown in Fig. 4. The binding energies associated with Ti $2p_{3/2}$ and Ti $2p_{1/2}$ were found to be 458.9 eV and 464.6 eV, respectively (Fig. 4a). The XPS of O 1s core electrons for the anatase TiO_2 crystals showed the binding energy of 530.17 eV, Fig.4b. The chemical state of these species suggests the growth of TiO_2 crystals on Ti substrates.

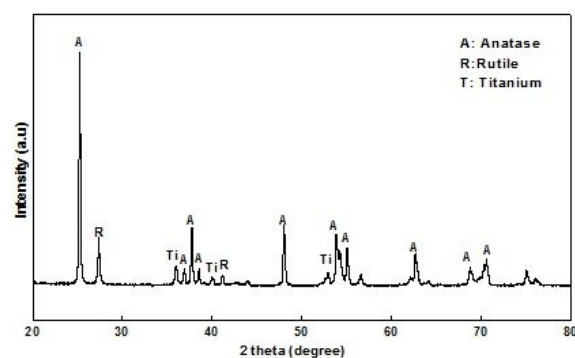


Fig. 3: XRD pattern of prepared TiO_2 / Ti film.

Decomposition of Clf By Uv and Uv / TiO_2 Photocatalysis

Fig. 5 shows photodecomposition kinetics of CLF by UV and UV/ TiO_2 in the presence and absence of dissolved oxygen. The Fig shows that the Kinetics of CLF decomposition well fits pseudo first-order reaction rate and photo-degradation of CLF was enhanced in the presence of TiO_2 / Ti catalyst. It was also observed from these experiments that UV-photolysis / photocatalysis of CLF was somewhat faster when the samples were saturated with O_2 -gas as compared to N_2 -saturated solutions. The results also shows that the decomposition rate constant of CLF were higher for O_2 – saturated solution than N_2 -saturated solution for UV-photolysis alone and for UV / TiO_2 photocatalytic processes. These results are similar to the results reported by Han and coworkers [20] where O_2 saturation of solution greatly enhanced UV-photolysis and photocatalytic degradation processes of *p*-chlorobenzoic acid. Since in UV / TiO_2 processes, the main oxidant involved in the degradation of CLF is the hydroxyl radical ($\cdot\text{OH}$) and dissolved oxygen facilitate its formation because it can accept photo - generated electrons, as shown by following series of reactions.

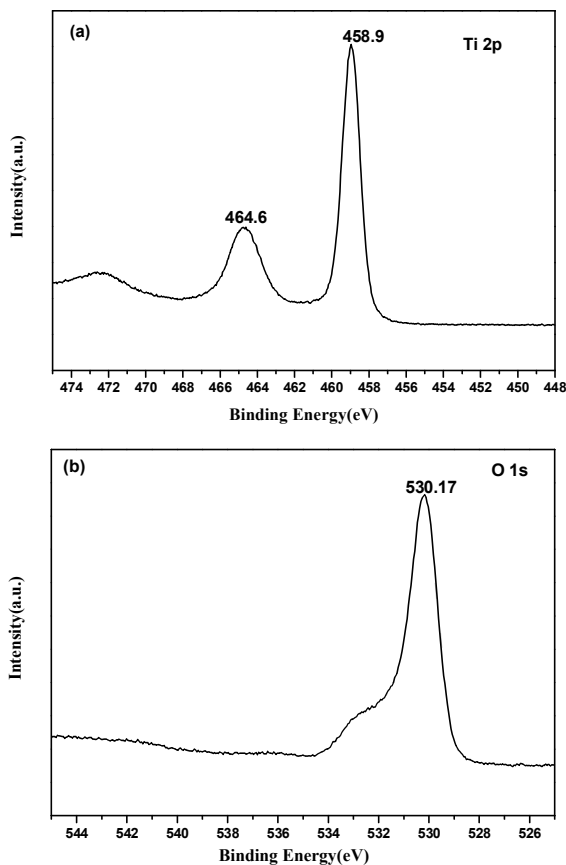


Fig. 4: XPS spectra of TiO_2 / Ti film (a) Ti 2p, (b) O 1s.

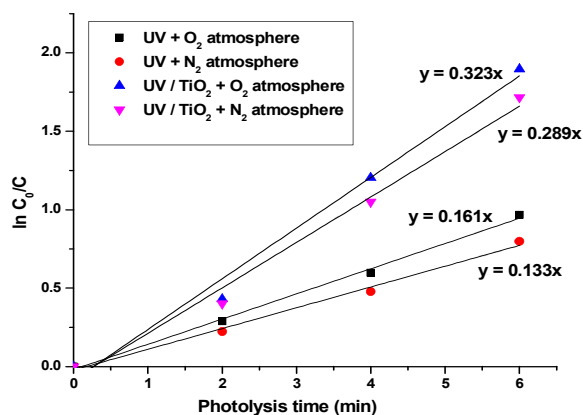
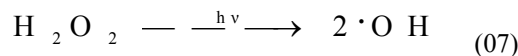
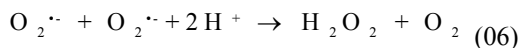
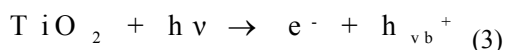


Fig. 5: Kinetics of CLF decomposition by UV and UV / TiO_2 in the presence and absence of dissolved O_2 .

In case of UV / TiO_2 photocatalysis,

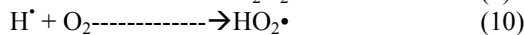
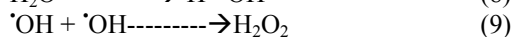


where h_{vb}^+ means holes in the valence band, while h_{tr}^+ represents trapped holes.

Furthermore, in case of direct UV-photolysis, clofibric acid after absorbing UV-radiations is promoted to an excited state. This molecule in the excited state has very short life time and thus returns to the ground state or decomposes to give a different molecule.

Decomposition of CLF by Vuv and Vuv / TiO_2 Photocatalysis

In case of VUV-photolysis of water, hydroxyl radical and other species are formed according to the following reactions:



Hydroxyl radical thus formed then reacts with CLF, as a result VUV photolysis is much more efficient than TiO_2 / UV process [20]. However the penetration power of 185 nm light in water is very short due to its high absorption coefficients (1.8 cm^{-1} at 25°C) [21]. The decomposition kinetics of CLF by VUV – processes as shown in Fig. 6 indicates that VUV / TiO_2 photocatalytic degradation was much more efficient as compared to VUV photolysis alone. The results also show that photolytic / photocatalytic degradation of CLF with O_2 slightly was higher than for N_2 saturated solution under both cases of VUV or VUV / TiO_2 techniques. Kinetic plots also show that photocatalytic reactions are much more efficient than any photolysis process. As mentioned earlier, in case of VUV and TiO_2 / VUV processes, the main specie responsible for degradation is hydroxyl radical. However, oxygen has low absorption coefficient at 185 nm [22] and low concentration in water, so oxygen itself is unable to absorb 185 nm light and form hydroxyl radical or ozone. So, bubbling of O_2 has no significant effect on degradation of CLF under VUV or VUV / TiO_2 processes.

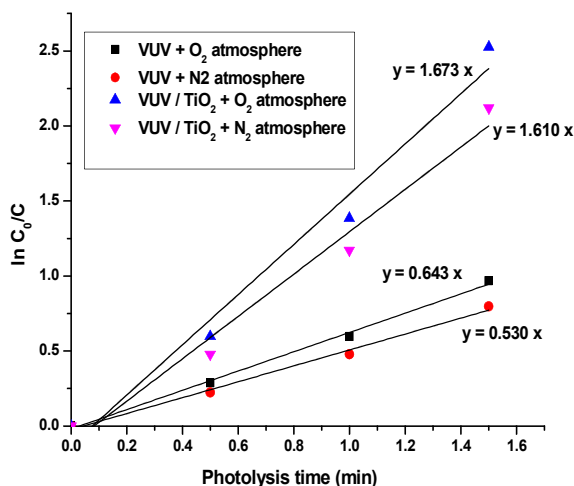


Fig. 6: Decomposition kinetics of CLF by VUV and VUV / TiO₂ in the presence and absence of dissolved O₂.

The kinetic parameters obtained from the applied AOTs for decomposition of CLF are summarized in Table-1.

Figures of Merit for the Applications of Advance Oxidation Technologies

AOPs are mostly energy driven processes, and thus operating cost are dependent on the electrical energy. Figs of merit based on electrical energy consumption of AOPs are necessary for their practical applications. Since the concentration of CLF is not very high so following Fig of merit is proposed.

Electrical Energy Per Order (e_{eo}). “Electric energy per order (E_{EO}) is the electric energy in kilowatt hours [kWh] required to degrade a contaminant C by one order of magnitude in a unit volume [e.g., 1 m³] of contaminated water or air”.

This Fig-of-merit is best used under cases where [C] is low (i.e., cases that are overall first-order in C) because the amount of electric energy required to bring about a reduction by one order of magnitude in [C] is independent of concentration C. Thus, same amount of electric energy will be consumed to decompose the contaminant concentration from 10 mg L⁻¹ to 1 mg L⁻¹ in a given volume as it would be consumed to reduce 10 μg L⁻¹ to 1 μg L⁻¹. E_{EO} can be defined as:

E_{EO} values can be calculated using the following formula [23];

$$E_{EO} = \frac{pt1000}{V \lg(C_i / C_f)} \text{ kWh / m}^3 / \text{order} \quad (11)$$

where, p is the rated power [kW] of the AOP system, V is the volume [L] of water or air treated in the time t [h] and log is the symbol for the decadic logarithm.

Since, $\log(C_i / C_f) = 0.4343k_1' t$, where t [min] is the reaction time in the reactor and k_1' is the first-order rate constant [min⁻¹]. So, equation (11) can be re-arranged as;

$$E_{EO} = \frac{38.4P}{Vk_1'} \quad (12)$$

where V is the batch reactor volume (L).

Table-1 shows comparisons of different AOPs applied in the present study for CLF degradation in terms of E_{EO} -values. As can be seen from Table 1, VUV/TiO₂ in addition to O₂ purging utilizes less energy and thus less cost to degrade CLF by one order of magnitude in a unit volume. On the other hand UV-alone with N₂ purging does considerable more expensive than others owe to the higher energy consumption in the removal of CLF.

Furthermore, the long term photo stability of synthesized material was also checked for potential practical applications. It can be seen from Fig. 7 that nearly 90 % of BZF was degraded in 8 min by UV/TiO₂ photocatalysis in the presence of oxygenated atmosphere and its activity almost remained same till the sixth run.

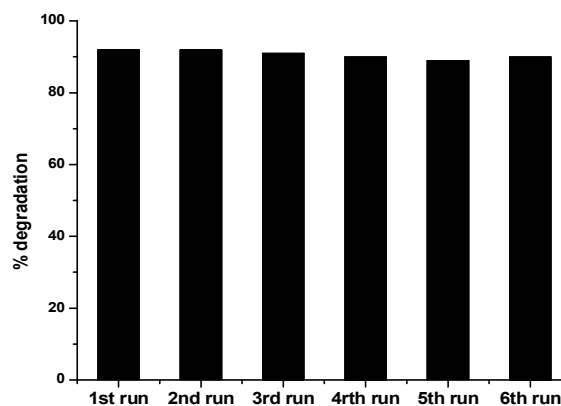


Fig. 7: The long term photostability of synthesized TiO₂/Ti photocatalyst.

Table-1: E_{EO} -values of applied AOTs for decomposition of CLF in aqueous media.

Applied AOTs	First-order rate constants k_1		E_{EO} values [kWh / m ³ / order]
	min ⁻¹	hr ⁻¹	
UV / O ₂	0.261 ± (1.5 × 10 ⁻³)	0.0043 ± (1.0 × 10 ⁻⁴)	893.0233
UV / N ₂	0.133 ± (1.5 × 10 ⁻³)	0.0022 ± (1.0 × 10 ⁻⁴)	1732.07
VUV / O ₂	0.643 ± (2.0 × 10 ⁻³)	0.0107 ± (1.5 × 10 ⁻⁴)	358.3092
VUV / N ₂	0.53 ± (1.5 × 10 ⁻³)	0.0088 ± (2.0 × 10 ⁻⁴)	434.7334
UV / TiO ₂ + O ₂	0.373 ± (1.5 × 10 ⁻³)	0.0062 ± (2.0 × 10 ⁻⁴)	617.6613
UV / TiO ₂ + N ₂	0.289 ± (3.5 × 10 ⁻³)	0.0048 ± (1.0 × 10 ⁻⁴)	797.1764
VUV / TiO ₂ + O ₂	1.673 ± (1.5 × 10 ⁻³)	0.0278 ± (1.5 × 10 ⁻⁵)	138.0451
VUV / TiO ₂ + N ₂	1.610 ± (1.0 × 10 ⁻³)	0.0268 ± (1.5 × 10 ⁻⁵)	143.2836

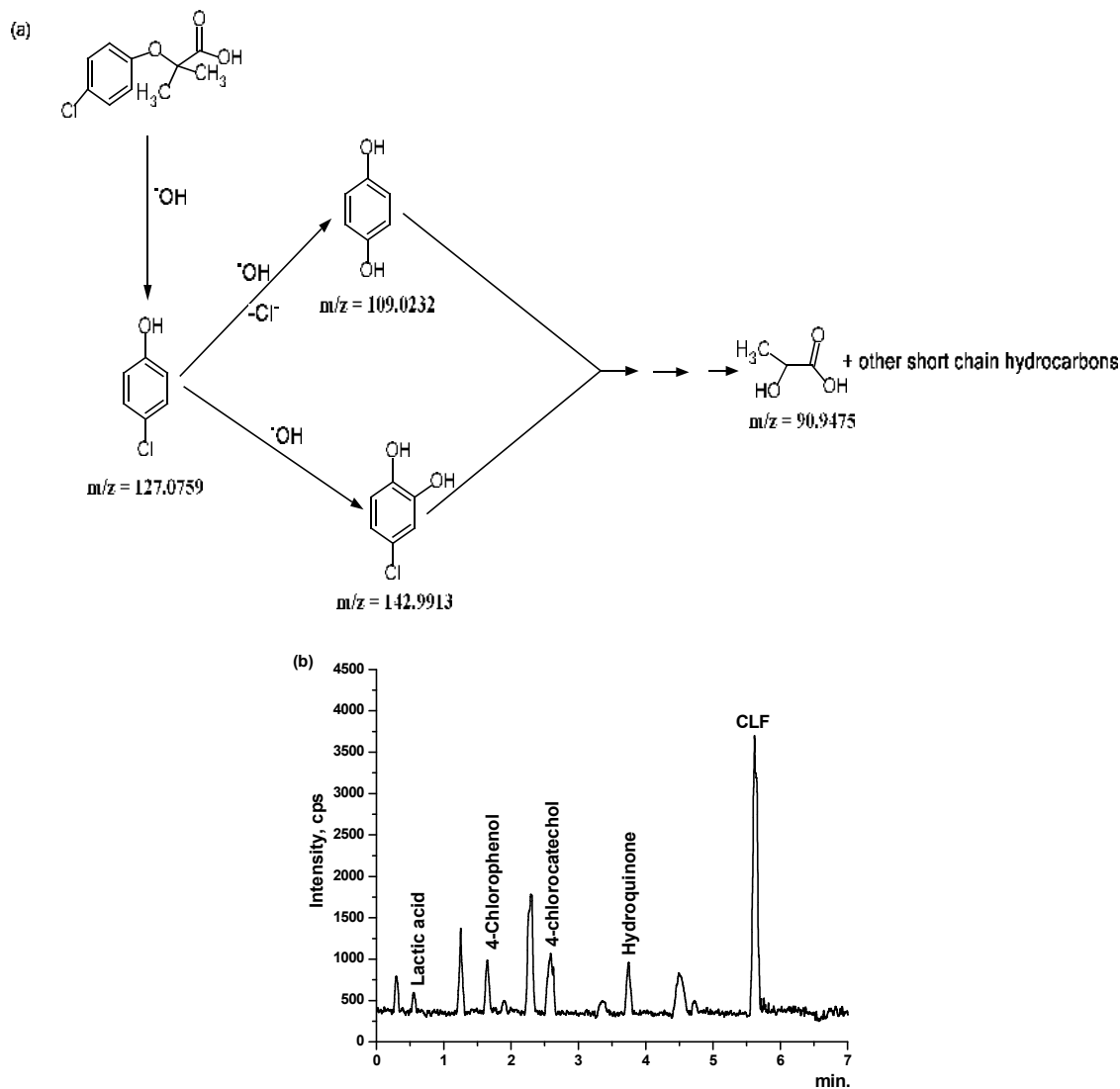


Fig. 8: Proposed degradation pathway for clofibric acid by VUV / TiO₂ process (a), total ion-chromatogram of the degradation byproducts of clofibric acid (b).

Evaluation of Photo-Degradation by-Products and Proposed Pathway

CLF samples obtained at different irradiation times of VUV exposures in the presence of TiO₂ film were then analyzed for CLF degradation products by UPLC- MS / MS and the obtained total ion chromatogram is shown in Fig. 8(a). The resulted

hydroxylated by-products may be due to attack of [•]OH radical at C-O bond of the clofibric acid. The peak that appear at (m/z) of 127.0759 shows the formation of chlorophenol. Sirés et al. [24] also proposed the formation of chlorophenol after oxidation of clofibric acid by fenton process. Further parallel attack of [•]OH radical on chlorophenol with the release of Cl⁻ results in the formation of

hydroquinone with m/z of 109.0234 as previously reported by Doll and Frimmel [25] also, and 4-chlorocatechol at m/z of 142.9913. The formation of lactic acid at m/z of 90.9475 confirms the degradation of clofibric acid to short chain hydrocarbons. Fig. 8 (b) shows a plausible pathway for degradation of clofibric acid by VUV / TiO_2 process. The peak areas of resulting byproducts are shown in Fig. 9. It can be seen that all the intermediates exhibited nearly identical trend. The peak area of 4-chlorophenol was much higher than the peak area of other intermediates, this might be due to the fact that initially there is greater generation of $\cdot OH$ and thus resulting in quick formation and destruction of chlorophenol. The peak area of lactic acid shows that it is accumulated slowly without apparent degradation initially however, at absorbed dose of 120 minutes it reached a maximum and then decreases.

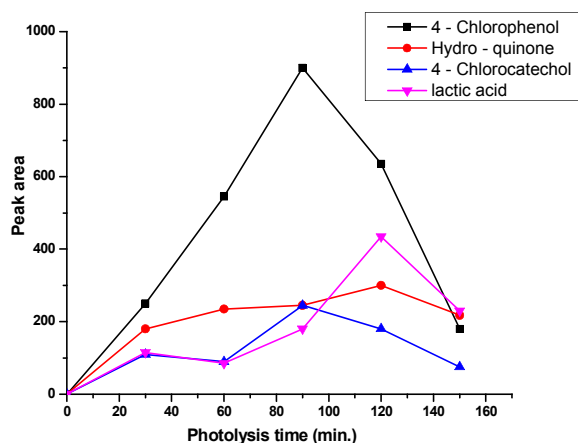


Fig. 9: Evolution and decay of clofibric acid intermediates detected by UPLC-MS/MS.

Conclusions

The degradation of clofibric acid as target pollutant was investigated with UV (254 nm), UV/ TiO_2 , VUV (185 nm) and VUV / TiO_2 photolysis / photocatalysis in the presence and absence of dissolved oxygen. The complete degradation of CLF during UV photolysis was reached in 5 min during UV/ TiO_2 photocatalysis, while during VUV / TiO_2 photocatalysis, the complete degradation was achieved in 1 min starting with the concentration of 5ppm. In the case of UV photolysis / photocatalysis, the degradation process was faster in the presence of dissolved molecular oxygen while in case of VUV photolysis / photocatalysis the dissolved oxygen has no significant role on the degradation process of CLF. VUV / TiO_2 with dissolved O_2 was found as the

most cost effective advanced oxidation process for the removal of CLF from aqueous media among the different AOPs applied in this study. All the applied AOPs follow *pseudo*-first order kinetics for the decomposition of CLF in aqueous media. During our study, four main by-products of CLF were identified.

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